# Nanoindentation as a Method for the Study of Irradiation Effects in Polymer Matrix Composites

M. M. Stevanovic

Materials Department, Vinca Institute, University of Belgrade, Serbia

stevanovicmomcilo@yahoo.com

***Abstract***

Unidirectional carbon fibres/epoxy resin composites gamma rays irradiated to doses from 4.8 to 27.2 MGy. Before and after irradiations and annealing at 180 and 250°C, the coupons are tested in the nanoindentation and delamination toughness tests. By nano indentation testing, the hardness and modulus of composite's phases have obtained. The priority aim was to establish and explain irradiation and annealing effects on hardness and modulus of composites phases; as well to emphasize the suitability of the obtained properties for studying irradiation and annealing effects on fracture mechanics parameters of tested composite, and to get the insight into the mechanisms inducing observed changes. Decrease of all properties of composite phases with increasing radiation dose has been observed. The critical strain energy release rate of delamination at the fracture initiation point, $G_{IC, INIT}$, has been adopted as main fracture mechanics parameter characterizing the interlaminar fracture resistance to delamination. Using matrix hardness to Young modulus ratio, calculated matrix plasticity, has been assessed according to Mil'man's approach, for the tested composites before and after irradiation and annealing. By analysis and mutual correlation of irradiation and annealing effects, obtained in nanoindentation and fracture mechanics tests, the established results have been explained and some insight to mechanisms of properties changes has obtained.

***Keywords***

*Nanoindentation; Hardness; Young Modulus; Mode I Tensile Tests; Strain Energy Release Rate; Mechanisms of Effects*

## Introduction

The scope of this paper is the radiation damage of polymer matrix/unidirectional fibres composites (PMC) especially the effects of irradiation and subsequent annealing on the fracture mechanics parameters and on the properties obtained by nanoindentation technique. Both applied testing methods are relatively new. In addition, an attempt has been made to emphasize the priorities and important role played by the application of nanoindentation tests in the study of radiation damage of the investigated composite.

The effects of ionizing irradiation on PMC properties represent a subject of widespread importance (Gordic et al., 2007; Sekulic et al., 2009). Data on irradiation effects on properties are available, but little knowledge exists on annealing effects. These effects have observed in many different cases (Gordic et al., 2007; Sekulic et al., 2009; Sekulic & Stevanovic, 2011) but the doubts remain on the dominating mechanisms of the phenomena. During the study of radiation and post-irradiation annealing effects, many authors followed the changes of matrix glass transition temperature $T_g$, by linking them to the chemical reactions such as chain scission and/or formation of cross links (Sekulic et al., 2009). However, it has been suggested that real situations connected with radiation effects on PMC are far more complex, due to high sensitivity of the elastomer matrix to its environment (oxygen) and thermosets to the resin system composition (Davenas et al., 2002).

Radiation and annealing effects have been explained generally by concurrent mechanisms: chain scission or cross-linking, gas products formation and evacuation (during annealing), changes of matrix plasticity or changes in fibre/matrix interface ability to transfer the load. The mechanisms of scission and cross-linking for polymethyl methacrylate subjected to various irradiation sources, such as low linear energy transfer (LET) radiation sources (MeV e-beams, $Co^{60}$ gamma-rays) and high LET ions (MeV $He^{+}$, $Ar^{+}$) have been investigated (Lee et al.,2003). Their results show that high LET irradiation produces high concentration of free radicals over many neighbouring molecular chains, facilitating track overlap and enhancing cross-linking over scission, while low LET affects only a single molecular chain, leading to chain scission. The authors of paper (Lee et al., 2003) quoted that both cross-linking and scission occur simultaneously

during irradiation of polymers, but the relative magnitude of cross-linking (gelling) to scission (degradation) depends upon polymer structure. The data (Bisby et al., 1977, Yates & Shisonaki, 1993; Schnabel et al., 1984; Kudoh et al., 1997; Lee, 1996;), however, showed that scission and cross-linking depend not only upon polymer structure, but primarily upon the energy deposited per unit track length or linear energy transfer (LET).

In this paper, the matrix and fibres hardness and Young's modulus and the critical strain energy release rate, as a measure of delamination (fracture) toughness of carbon fibre/epoxy resin composites, irradiated by gamma-ray doses from 4.8 to 27.2 MGy, have been studied. Hardness and Young's modulus were determined by method of nanoindentation (Sekulic & Stevanovic, 2011), while the strain energy release rate was established by tensile tests of double cantilever coupons (Sekulic et al., 2009). The same properties of irradiated coupons have been measured after thermal treatments at 180 and 250°C in vacuum. In this way, the effects of irradiation to various doses and thermal treatments on hardness and Young's modulus of matrix and fibres in the tested carbon/epoxy composites were established. The variations of the cited values with irradiation and annealing were compared with the results of delamination fracture toughness, having in mind the variation of glass transition temperature $T_g$ values. Using the obtained results of hardness and Young's modulus, $H_m/E_m$ ratio values for the tested composite matrices have been calculated before and after irradiation and annealing, using Mil'man's approach (Mil'man et al., 1999, Mil'man, 2008). Based on this, the plasticity of the matrix has been evaluated and an attempt has been made to assess the contribution of the plasticity changes mechanism to the variation in matrix properties.

The aim of the presentation was to establish irradiation and annealing effects on the properties of composite components, which is particularly important for carbon-carbon composites. Apart from this, the more important goal was to emphasize the suitability of properties, obtained by nanoindentation, to study other irradiation and annealing effects, but also to get insight into the mechanisms inducing these property changes. Special attention has been paid to the elucidation of the role of polymer matrix plasticity change's mechanism in polymer matrix composites.

The paper embraced the presentation of the fundamentals of Mil'man's theoretical approach for assessment of matrix plasticity by using its hardness ($H_m$) and Young's modulus ($E_m$). The aim was to establish the contribution of plasticity change mechanism to the changes of PMC properties due to irradiation and annealing. It has done successfully in case of the effects on delamination toughness of these composites. This is an excellent example that shows how the interaction between different approaches offers a fruitful source of data improving our understanding of the studied phenomena.

## Experimental

The laminated plates have been prepared from unidirectional high strength carbon fibres (Twaron HTS)/epoxy prepreg- HexPly 6376-NCHR, supplied by HEXCEL. Epoxy resin in the prepreg was based on the tetraglycidyl-p-aminophenol derivative of metilene dianiline. The plates have been prepared by hot (175°C, 2h, 700 kPa) platen pressing and the laminate sheets of the composites before and after irradiation have been cut into coupons.

### *Irradiation, Annealing*

The $^{60}$Co gamma-ray irradiations, with a dose rate of 12 kGy/h, have been conducted in air, at an ambient temperature, up to the doses from 4.8 to 27.2 MGy. One part of non-irradiated and irradiated coupons has been annealed for two hours, under vacuum, at the temperatures of 180 and 250°C.

### *Tests Methods*

#### *1) Nanoindentation Tests*

The hardness and Young's modulus of matrix and fibres in unidirectional carbon fibres/epoxy composites were measured using the nanoindentation technique. Nanoindentation tests have performed in the Max Planck Institute, Stuttgart (Burghard, et al., 2007) with a Digital Instruments Nanoindenter. By using sensors with high resolution for continuous recording and measurement of the load ($P$) and the indenter displacement ($h$), the nanoindentation instrument performed measurements of present phase's properties with high precision. Matrix width between fibres (7 μm diameter) had dimensions higher than 6 to 8 μm (Fig.1.), reliable $H$ and $E$ values related only to the matrix or the fibre have been obtained by nanoindentation. These results have not been influenced by the presence of the

other phase and they are very useful tool to conduct study of irradiation effects in continuous fibre PMC.

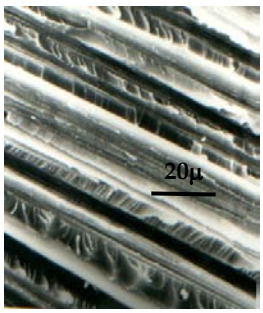



FIG.1 SEM MICROGRAPHS OF UDC SHEAR FRACTURE

Load range in the test was from 0.01μN up to 12 mN (with resolution of 0.1 μN on 100 μN) and that of penetration depth from zero to 1μm (with resolution of 0.02 nm) (Fig.2.). Nanoindentation tests have been performed using Berkovich-diamond indenter, with the trihedral pyramid tip and a nominal tip diameter of 50 nm, by applying the Oliver-Pharr method (Oliver & Pharr, 1992).

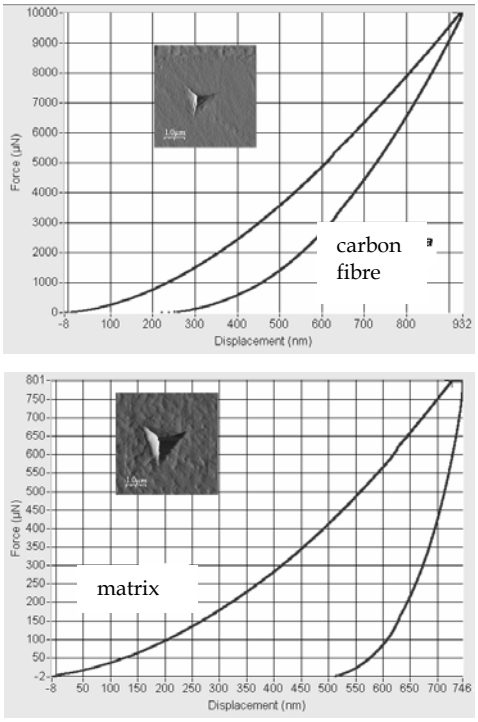



FIG. 2 LOAD PENETRATION DEPTH PLOTS

The indenter tip was at the right angle to the fibres direction onto the specimen of a sheet shape (dimensions 2x7x10 mm), with plane, smooth and parallel surfaces. The hardness and Young's modulus have been derived from the measured load-contact depth curves, following the OP procedure. Both measured values are expressed in GPa, as the mean values of n=16 measurements, with standard deviation $\sigma$ and standard error $S_{ERR} = \sigma / \sqrt{n}$ (Tidestrom, et al., 1959). The error bars in our figures for indentation properties obtained by nanoindentation, are equal to standard errors.

### 2) *Delamination Toughness Tests*

In unidirectional fibres reinforced plastics, the value of delamination critical strain energy release rate $G_{IC}$ has been used as a measure of fracture toughness. The Mode-I double cantilever beam (DCB) test was used for the determination of $G_{IC}$ values. The results of the critical strain energy release rate, $G_{IC}$, have been used mostly for comparative purposes. Many researchers have investigated delamination fracture toughness of composite laminates for Mode-I loading (Schön et al., 2000; de Morais et al., 2002; Pereira & de Morais, 2004). To the best of our knowledge, the only data on irradiation effects of $G_{IC}$ values are those presented by the author's papers published recently (Sekulic et al., 2009; Sekulic & Stevanovic, 2011).

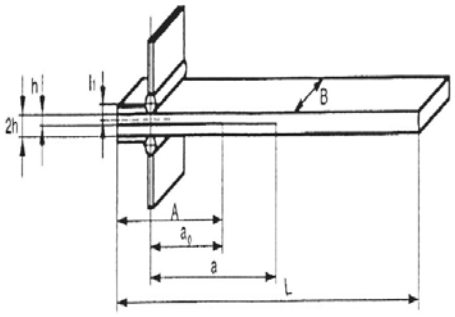



FIG. 3 GEOMETRY OF DCB SPECIMEN. B – SPECIMEN WIDTH, 2h – SPECIMEN THICKNESS, $a_o$ – INITIAL DELAMINATION LENGTH, a – TOTAL DELAMINATION LENGTH, A– INSERT LENGTH, L – SPECIMEN LENGTH AND $l_1$ – DISTANCE FROM THE CENTRE OF PIANO HINGE AXIS TO THE MID-PLANE OF THE SPECIMEN

The DCB specimens (Fig. 3) have been cut from the plates with dimensions 3.6×25×125 mm. A 13μm thick PTFE film, inserted in the plate's mid-plane, has been used to generate the starter crack. Piano hinges have glued to the specimens for load transmission. Both lateral edges of specimens have been coated with white paint and several marks have been made to facilitate the monitoring of crack position. The DCB test has been performed on a Universal Testing Machine INSTRON M 1185 (in the Nuclear Institute Vinca, Belgrade) at a

crosshead speed of 1 mm/min, at the room temperature and atmospheric pressure.

The force and the opening displacement signals of the testing machine have been recorded on the chart. Delamination length has been measured visually on the specimen edges. The point, at which the onset of delamination movement from the starter film occurred on the edge of the specimen, was marked on the force-displacement curve. The pre-crack loading has been stopped at a delamination length increment of 5 mm.

The position of the tip of the pre-crack was marked on both edges of the specimen after unloading. Data processing has been carried out according to the Method B of ISO 15024 standard document. The critical energy release rate $G_{IC}$ was calculated using equation

$$G_{IC} = \frac{3m}{2(2h)} \left(\frac{P}{B}\right)^2 (\delta C)^{2/3} \quad (1)$$

where $P$ denotes the load, $\delta$ is the opening displacement, B specimen width, and 2h specimen thickness. The compliance $C$ is equal to $\delta/P$ and m represents the slope of $(BC)^{1/3}$ versus $a/2h$ plot. The $G_{IC}$ parameter for non-irradiated, irradiated and annealed coupons has been calculated as the mean value from 10 different propagation distances ($G_{IC,MEAN}$) (Figs. 9, 10) Their standard deviation is the measure of the span between $G_{IC}$ values of the onset and the end of crack propagation, which can be seen from the R curves (Fig. 10). The $G_{IC}$ value for each of ten propagation points has been calculated as the mean value from every five coupon.

### 3) *Glass Transition Temperature*

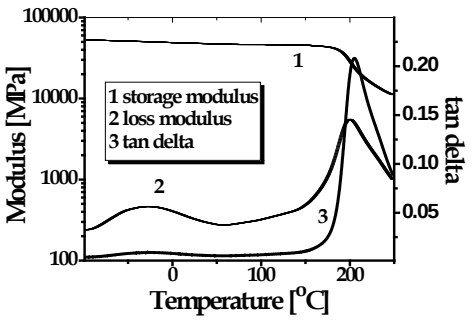



FIG. 4 CHARACTERISTIC DMA DIAGRAM

The matrix glass transition temperature ($T_g$) values have been determined by DMA in the single cantilever mode, using TA Instruments Multi-Frequency 2980 Dynamic Mechanical Analyzer. The tests have been performed in the temperature range from -100 to 250°C and the storage modulus, loss modulus and tan delta curves were recorded (Fig.4). $T_g$ has been deduced from position of the highest temperature peak on the loss modulus curve.

## Nanoindentation Results

### *Irradiation Effects*

The results of nanoindentation measurements of matrix and fibre property changes, due to irradiation and annealing effects have been presented on figures as the mean values, with error bars equal to standard error $S_{ERR} = \sigma/4$ (Tidestrom, et al., 1959). Nanoindentation has provided reliable values of hardness $H$ and Young's modulus $E$, of the fibre and the matrix (Figs. 5 and 6), free from influence of the presence of the other phase. The fibres Young's modulus obtained in nanoindentation test is the transverse (radial) modulus of carbon fibres $E_2$. Low experimental value (20.7 GPa) (Fig. 5) compared to the fibre longitudinal (axial) modulus ($E_1$) value is expected. For high strength carbon fibre, $E_1/E_2$ ratio is higher than 10 (Hull & Clyne, 1996). Reynolds et al. (1973) determined $E_2$= 30 GPa for the transverse modulus of high strength carbon fibres, but he used a dynamic method of ultrasonic wave propagation through the material. Our test is static. The $E_2$ value reported is also lower than the carbon fibre value (27.0 to 30.5 GPa) obtained by nanoindentation of carbon-carbon composite (Diss et al., 2002; Marx & Riester, 1999). But, carbon-carbon composites have been obtained with high modulus carbon fibres. The recorded $E_2$ value has decreased with higher irradiation dose (Fig.5), indicating small radiation damage in the interlayer between graphene planes of the tested carbon fibre.

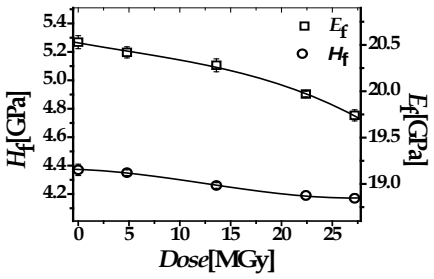
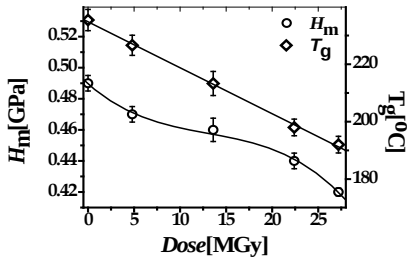



FIG.5 FIBRE'S HARDNESS AND YOUNG'S MODULUS AS FUNCTIONS OF DOSE

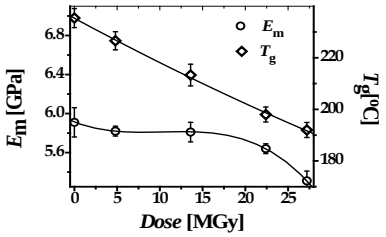
The properties of practical interest are those of matrix, because the matrix, as well as the fibre/matrix

interphase, has been noticeably influenced by gamma irradiation.

The matrix $H_m$ and $E_m$ values, obtained by nano-indentation, decrease with the increase of irradiation dose (Fig.6). That is pronounced at higher doses, of 22.4 and 27.2 MGy. Since the performed irradiation of the tested polymers has followed by lowering of the glass transition temperature $T_g$, these changes of matrix properties have been ascribed to the mechanism of chain scission, as a dominant mechanism of radiation damage.




a.




b.

FIG. 6 MATRIX HARDNESS (a), YOUNG'S MODULUS (b) AND $T_g$ VALUES AS FUNCTIONS OF IRRADIATION DOSE

Hardness enhancement due to cross-linking mechanisms in polystyrene irradiated with high-energy ion-beams has been observed by Lee et al. 1997. The degradation of hardness has occurred when PMMA has subjected to low LET ionizing irradiation, such as electron beam or gamma rays (Lee et al. 1999). The same has been revealed for gamma-ray irradiation of epoxy matrix in our measurements.

The performed irradiation in this paper on carbon/epoxy composites represent irradiation with low linear energy transfer-LET (Lee et al., 1999), and our results are in a full agreement with the nowadays widely accepted comprehension of irradiation effects in polymers (Lee et al., 1993, 1996, 1997, 1999). The implication of the study presented in paper (Lee et al. 1993) is that the hardness of PMMA increases significantly with the increasing $Ar^+$ irradiation flux. At higher LET, higher extent of cross-linking has been achieved at equivalent irradiation dose or equivalent deposited energy per unit mass of material. For high LET irradiation, the hardness has shown to be a measure of the extent of cross-linking (Lee, 1996).

In two papers (Mil'man et al., 1999, Mil'man, 2008) the dimensionless parameter $\delta_H$ has been defined as

$$\delta_H = \varepsilon_p / \varepsilon_t \quad (2)$$

where $\varepsilon_p$ and $\varepsilon_t$ are the mean values of plastic and total material strain in the sample, on the indenter-surface contact. The $\delta_H$ parameter enables characterization of the material's plasticity. It has been calculated from the values of hardness $H$, Young's modulus $E$ and Poisson's ratio $\nu$.

During instrumented nanoindentation, the plasticity characteristic is given by relation

$$\delta_A = A_p / A_t \quad (3)$$

where $A_p$ and $A_t$ are the mean values of plastic and total strain work, respectively. For materials having $\delta_H > 0.5$, $\delta_A$ is approximately equal to $\delta_H$. In such a case, theoretical equation is

$$\delta_A \sim \delta_H = 1\text{-}10.2(1\text{-}\nu\text{-}2\nu^2)(H_N / E) \quad (4)$$

and it is compatible to the experiments with Berkovich indenter (Mil'man, 2008), that has been used in our indentation tests. (The subscript N refers to nanoindentation.) Eq. (4) implies that the material's plasticity is higher for lower $H$/E ratio. $H/E$ ratio is, consequently, a measure of material's plasticity, and these two variables are reciprocal, under the assumption that the Poisson ratio is constant during irradiation and annealing.

The $H_m/E_m$ ratio of non-irradiated and irradiated samples (Fig.7) has calculated from $H_m$ and $E_m$ results, presented in Fig.6. The aim was to assess the matrix plasticity of the tested samples, i.e. the contribution of the mechanism of matrix plasticity change to the variation in changes of unidirectional composite (UDC) properties.

***Thermal Treatment Effects***

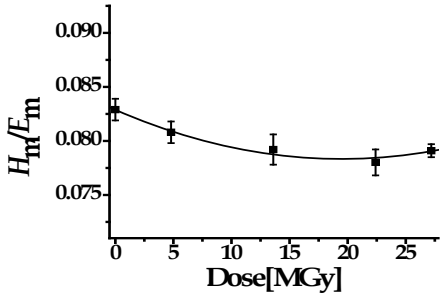
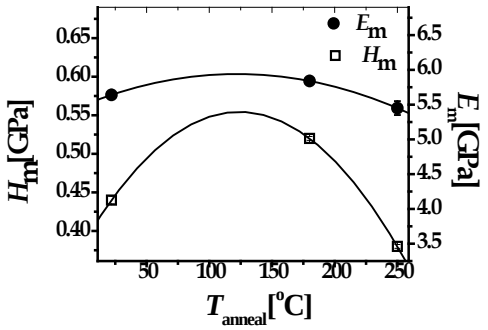
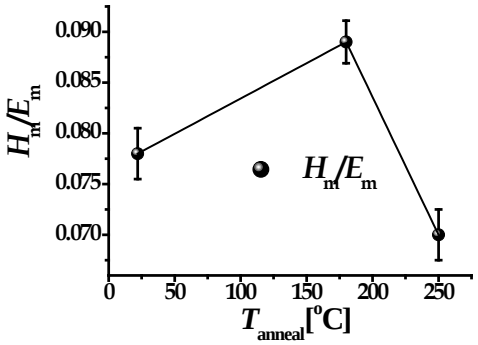



FIG. 7 MATRIX HARDNESS TO YOUNG'S MODULUS RATIO AS A DOSE FUNCTION

The effect of thermal treatments on irradiated samples has been studied by determining the matrix hardness $H_m$ and Young's modulus $E_m$ of UDC samples, irradiated with the dose of 22.4 MGy (Fig.8.a). The study has been continued by calculation of $H_m/E_m$ ratio and by the assessment of the matrix plasticity changes during thermal treatment at180 and 250°C (Fig. 7.b).




a.




b.

FIG. 8 $H_m$ AND $E_m$ (a) AND MATRIX $H_m/E_m$ RATIO VALUES (b) BEFORE AND AFTER THERMAL TREATMENTS FOR SAMPLES IRRADIATED WITH THE DOSE OF 22.4 MGY

After thermal treatment at 180°C, $H_m$ values of irradiated samples are higher than that before thermal treatment (Fig. 8a), while the glass transition temperature $T_g$ values have not changed (Fig. 12.b). After annealing at 250°C, the $H_m$ values of irradiated samples are somewhat under the level of untreated samples (Fig.8.a), however, $T$g values continue to increase (Fig. 13.b). The $H_m/E_m$ ratio value after thermal treatment at 180°C is higher, but after annealing at 250°C, it is lower than that before thermal treatments (Fig.8.b). It means that plasticity of matrix decreases after annealing at 180°C and increases after annealing at 250°C.

## Delamination Strain Energy Release Rate

### *Irradiation Effects*

Variations of $G_{IC}$ values with irradiation and annealing have been correlated with irradiation doses and glass transition temperature values (Sekulic et al., 2009). The observed effects on $G_{IC}$ have been explained in details by concurrent mechanisms: chain scission or cross-linking, gas products formation and evacuation (during annealing), changes of matrix plasticity or changes in fibre/matrix interface ability to transfer the load. All of these mechanisms are possible, and some of them are present, but the dominant one induces changes of the given property. In assessing the dominating mechanisms of irradiation and annealing changes, the $G_{IC,INIT}$ values of crack initiation, from the pre-crack tip, have been considered as the only true interlaminar property (de Morais et al., 2002; Pereira & de Morais, 2004).

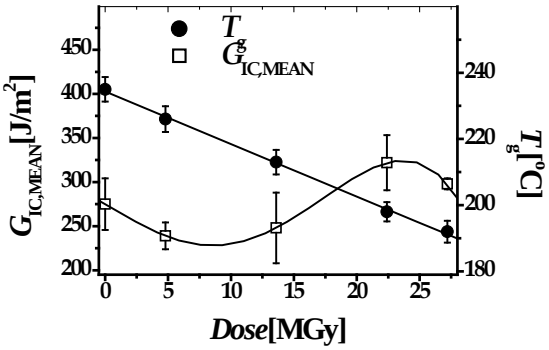



FIG. 9 $G_{IC,MEAN}$ AND $T_g$ VALUES AS A FUNCTION OF DOSE

The $G_{IC,MEAN}$ and $T_g$ values as a function of irradiation dose (Fig. 9) show that after 4.8 MGy dose, $G_{IC,MEAN}$ decreases, but after 13.6 MGy, it starts to increase up to the maximum at 22.4 MGy, and after that decreases again. However, $T_g$ values decrease linearly, from the value of non-irradiated sample to the obtained irradiation dose of 27.2 MGy. $T_g$ values follow the $G_{IC,MEAN}$ change trend only when it is decreasing. For these ranges $G_{IC,MEAN}$ changes can be ascribed to chain scission mechanism. For the dose interval where the irradiation induced changes of $G_{IC,MEAN}$ and $T_g$ are of the oposite sign, $G_{IC,MEAN}$ is not ascribed to the scission mechanism, meaning that the reason for these changes has to search in some other mechanism. This search has been started by the analysis of R-curves of $G_{IC,MEAN}$ versus crack propagation distance $a$ (Fig. 9).

R curves shape of non-irradiated coupons and that irradiated to the lowest dose are the same (Fig. 9). These delamination resistance curves are atypical (according to the criteria given in the ISO 15024 standard) by displaying the decreasing resistance to crack propagation with the growth of delamination length. R-curves for the coupons irradiated to higher

doses are typical delamination R curves, showing the increasing delamination resistance with the increase of delamination length.

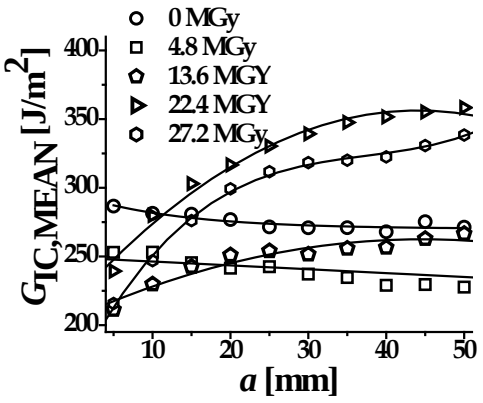



FIG. 10 R-CURVES OF $G_{IC,INIT}$ - PROPAGATION DISTANCE

It is evident (Fig. 10) that the span between $G_{IC,MEAN}$ values at the initiation point ($G_{IC,\ INIT}$) and at the end point of the crack propagation ($G_{IC,END}$), for coupons irradiated to higher (than 13.6 MGy) doses, is considerably high (Fig. 10). According to (Pereira & de Morais, 2004), when the span between $G_{IC,INIT}$ and $G_{IC,END}$ values becomes high enough, it means that $G_{IC,MEAN}$ values are influenced, as well, by a pronounced fibre bridging (de Morais et al., 2002; Brunner & Blackman, 2006).

The appearance of the fibre bridging has been seen by the visual observation of delaminated surfaces of the coupons irradiated with the higher doses. It means that numerical $G_{IC,MEAN}$ values for the doses higher than the mentioned limit have increased due to phenomenon of fibre bridging, during crack propagation. Due to this phenomenon, it is not possible to assess the irradiation effect based on those values. For such cases, it is recommend (Pereira & de Morais, 2004) to use $G_{IC,INIT}$, the values at the crack initiation point (i.e. at end of pre-crack point), as the single "true interlaminar characteristic". It is logical that the $G_{IC,INIT}$ value is independent on the delamination inter-surface characteristics. By adopting the explained approach, $G_{IC,\ INIT}$ values have been used in the assessment of irradiation and annealing effects.

By comparing the $T_g$ - $G_{IC,\ MEAN}$ (Fig. 9) and $T_g$ - $G_{IC,INIT}$ (Fig. 11) versus dose plots, it can be stated that after irradiation, with the all doses except those at 13.6 and 22.4. MGy, all three $G_{IC,MEAN}$, $G_{IC,INIT}$ and $T_g$ values are lower than those before irradiation. Irradiation up to 22.4 MGy dose causes the decrease of $T_g$ values and the increase of the mean $G_{IC,\ INIT}$ value (Fig.11.). Generally, for all doses except 22.4 MGy, it has been stated that the chain scission is the dominant mechanism responsible for mean $G_{IC,\ INIT}$ value.

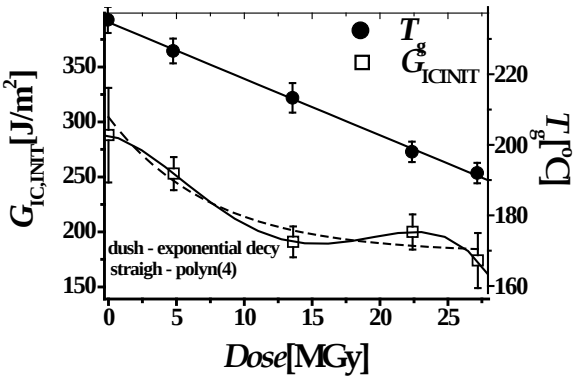
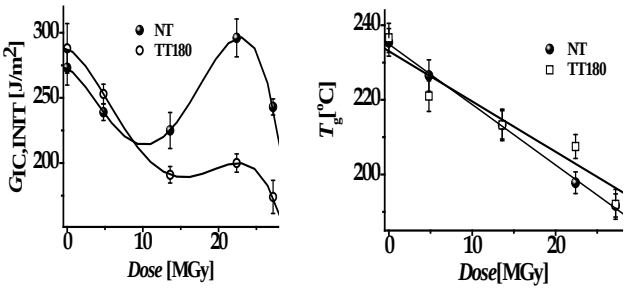



FIG. 11 $G_{IC,INIT}$ AND $T_g$ VALUES AS A FUNCTION OF DOSE

The change of mean $G_{IC,\ INIT}$ value during irradiation up to dose of 22.4 MGy has been ascribed, as a hypothesis, to the matrix plasticity increase (Seculic et al., 2009). The analysis of the results obtained by nanoindentation and their correlation with fracture mechanics results, has justified this hypothesis fully.

### *Annealing Effects*

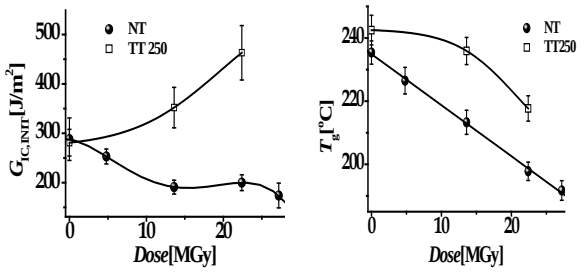
From R-curves of annealed coupons R-curves (Sekulic & Stevanovic, 2011), it has been observed that span $G_{IC,\ INIT}$ to $G_{IC,\ END,}$ for the higher irradiation doses, is high enough, too. It means that the contribution of the fibre bridging to the rises of $G_{IC,MEAN}$ values, before and after the thermal treatments, is evident, as well. It has been the main reason why our attention has directed to the variation of $G_{IC,\ INIT}$ values with the dose, as well, before and after the thermal treatments (Figs. 12. and 13.).The annealing at both temperatures, has carried out after irradiation at doses higher than 13.6MGy, causing changesof $G_{IC,INIT}$ (a) and $T_g$ (b) values after the thermal treatments at both annealing temperatures, 180 and 250°C.




a. b.

FIG. 12 $G_{IIC,INIT}$ (a) AND $T_g$ (b) VALUES BEFORE AND AFTER THERMAL TREATMENT AT 180°C

During the annealing at 180°C, $G_{IC,\ INIT}$ values of coupons irradiated with doses higher than 13.6 MGy, manifested decrease (Fig12.a), while $T_g$ values have not been affected (Fig.12.b). The $G_{IC,\ INIT}$ values of coupons irradiated to 13.6 -22.4 MGy have increased during the annealing at 250°C.




a. b.

FIG. 13 $G_{IIC,INIT}$ (a) AND $T_g$ (b) VALUES BEFORE AND AFTER THERMAL TREATMENT AT 250°C

This increase has not attributed to the cross linking of the polymer chains, because to the progressive rise of $G_{IC,\ INIT}$ values (Fig. 13.a) corresponds the decrease of the $T_g$ values, of annealed at 250°C coupons with higher irradiation dose(Fig. 13.b). The changes of $G_{IC.INIT}$ values, due to the thermal treatment, as well as, with the irradiation, have explained more properly by following the matrix plasticity change.

## Correlation of Properties

The study has been continued by calculation of $H_m/E_m$ ratio and assessment of matrix plasticity changes during thermal treatments at 180 and 250°C (Fig.8.b). The $H_m/E_m$ ratio for the samples, irradiated with the dose of 22.4 MGy calculated, using the values from Fig.8a, equals 0.078±0.001 before anneals. After the annealing at 180°C, the $H_m$ values of irradiated samples are higher than those before thermal treatment (Fig. 8a), while glass transition temperature $T_g$ values remain the same (Fig.12.b). In case of 180°C treatment, $H_m/E_m$ ratio is higher (0.090 ± 0.001), but after annealing at 250°C it is lower (0.07 ±0 .002) than before the treatments (Fig. 8.b). The 180°C treatment has led to higher $H_m/E_m$ ratio, to plasticity reduction, as well, to decrease of $G_{IC,\ INIT}$ values, as it has stated in the reference (Reis & Ferreira, 2006). The $H_m/E_m$ ratio has decreased during the annealing at 250 °C (Fig. 8.b) and induced the matrix plasticity increase, thus causing lower $H_m$ and higher the delamination toughnessvalues, $G_{IC,\ INIT}$.

The variation of matrix hardness values with increasingirradiation dose, has compared to change of $G_{IC,\ INIT}$, as anappropriate measure of delamination toughness (Fig.14). Having in mind standard errors, the decreasing trends of matrix hardness and of $G_{IC,\ INIT}$, with rise of irradiation dose, are similar (straight line in Fig. 14). However, the mean value of $G_{IC,\ INIT}$ shows local increase after the dose of 22.4 MGy (dashed line in Fig.14). The plasticity of the matrix has followed, through $H_m/E_m$ ratio, of irradiated samples, with increasing irradiation dose. The aim was to assess the contribution of mechanism of matrix plasticity change to the variation of $G_{IC,\ INIT}$ values.

For irradiation doses over 13.6 MGy, the mean value of$H_m/E_m$ shows evident decrease, compared to a the non-irradiated sample, indicating higher matrix plasticity.

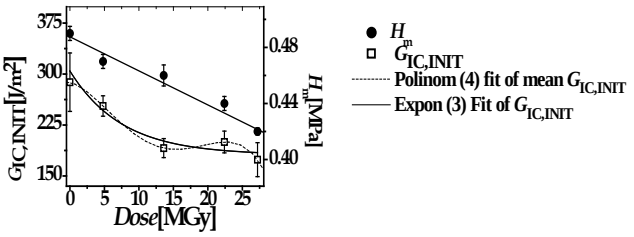



FIG. 14 $G_{IC,INIT}$ AND $H_m$ VALUES AS A FUNCTION OF IRRADIATION DOSE

Coupons irradiated with the dose of 22.4 MGy manifested the lowest $H_m/E_m$ ratio, i.e. the largest increase of the matrix plasticity. Simultaneously, $T_g$ value has not decreased. That is why the ascent of mean $G_{IC,\ INIT}$ value after irradiation dose of 22.4 MGy has been ascribed to the mechanism of matrix plasticity increase.

## Conclusions

Hardness and modulus values of two phases present in continuous carbon fibres/epoxy resin composite have been obtained by nanoindentation testing. The first aim of the study was to establish and explain irradiation and annealing effects on the hardness ($H$) and modulus ($E$) of composites phases. The decrease of all properties ($H_m$, $E_m$, $H_f$, $E_{2f}$) with increasing radiation dose has been observed. The degradation of matrix properties, due to irradiation, has been ascribed to the chain scission mechanism, as it was widely accepted for many matrix properties decreases due to low LET irradiation. The decrease of transverse fibre modulus during irradiation has been attributed to the some radiation damage induced in the fibre interlayer between graphene planes.

Because of high $G_{IC.INIT}$ to $G_{IC.END}$ span of R curves, for composite coupons irradiated to higher doses, and the evidence of the fibre bridging on fracture surfaces of

delaminated surfaces, it has accepted that $G_{IC,INIT}$ is the main fracture mechanics parameter characterizing the interlaminar fracture resistance to delamination in these composites. This parameter has been adopted as the only true interlaminar characteristic. The values of $H_m$ and $E_m$ have been used during the study of irradiation and annealing effects on the fracture mechanics parameters and other matrix properties of the tested composites. During this study, the aim was to get the insight into the mechanisms inducing these properties changes. By using the values of matrix $H_m/E_m$ ratio as a measure of matrix plasticity, according to the Mil'man's theoretical approach, the matrix plasticity has been assessed for the tested composites before and after irradiation and annealing.

Below have cited conclusions on the mechanisms of irradiation and annealing effects that have been deduced. The matrix plasticity change mechanism, besides chain scission one, has been accepted as the mechanism influencing properties such as $G_{IC,INIT}$ and matrix hardness decrease with the irradiation. In cases of irradiation with 22.4 MGy dose and annealing at 250°C, matrix plasticity increase was determined as the dominant mechanism. The $G_{IC,INIT}$ decrement during annealing at 180°C for coupons irradiated with doses higher than 13.6 MGy has been ascribed to the mechanism of matrix plasticity decrease.

## REFERENCES


Bisby, R. H. et al. (1977) LET Effects in Radiation-Induced… Papain Inactivation, Faraday Discussion of Chemical Society 237-247.

Brunner, A.J. et al. (2006) Calculating Damage Parameter and Bridging Stress from $G_{IC}$ Delamination Tests on Fibre Composites, Compos. Sci. Technol. 66 (6) 785-795.

Davenas, J et al. (2002) Ionising Radiation Stability of Polymers, Nuclear Instruments Methods and Physical Research, Section B: 191(1-4) 653-661.

Morais, A.B.et al. (2002) Mode-I Interlaminar Fracture of CFCEC, Composite Science and Technology, 62, 679-686

Diss, P. et al. (2002) Sharp Indentation Behaviour of C-C Composites, Carbon, 40, 2567-2579.

Egusa, S. et al. (1985) Annealing Effect on the Mechanical Properties on Organic Properties…, Journal of Nuclear Materials, 127(2-3) 146-152.

Gordic, M.V.et al. (2007) Strain Energy Release Rate in CFERC, Materials Science Forum, 555, 515-519.

Hull, D. et al. (1996) Introduction to Composite Materials, Cambridge University Press, Cambridge p.11.

Kudoh, H., et al. (1997) High Energy Ion Irradiation Effect on Polymer Materials. LET Dependence…, Radiation of Physic and Chemistry 50 (3) 299-302.

Lee, E.H et al. (1993) Hardness Measurements of $Ar^+$-Beam Treated Polyimide by Depth-Sensing ultra Low Load Indentation, Jornals of Matererial Research 8 (2) 377-387.

Lee, E.H. et al. (1997) Hardness Enhancement and Cross-Linking…, Materials Science Forum 248/249, 135-146.

Lee, E.H. (1996) Polyimide. Fundamental Aspects and Technological Applications, Dekker, New York

Lee, E.H et al. (1999) LET Effect on Cross-Linking/ Scission…, Radiation of Physics and Chemistry 55, 293-305.

Marx, D.T. & Riester, L., 1999, Mechanical Properties of C-C Composite…, Carbon, 37(11) 1679-1684.

Mil'man,Y.V.(1999) Indentation of Materials, Powder Metallugy of Metal and Ceramics 38, 396-402.

Mil'man, Y.V. (2008) Plasticity Characteristic Obtained by Indentation, Journal of Pysics, D. Applied Physics 41(7) 41 074013 (9pp) doi: 10.1088/0022-3727/41/7/074013.

Oliver, W. C. & Pharr, G.M. (1992), Hardness Measurement…, Journal of Materials Research, 7 (6) 1564-1583.

Pereira, A.B. & de Morais, A.B. (2004), Mode I Interlaminar Fracture..., Composite Science and Technology 64 (13-14) 2261-2270.

Reis, J.M.L. & Ferreira, A.J.M. (2006) Freeze-Thaw and Thermal Degradation … of Carbon, Construction of Building Materials, 120, 888-892.

Reynolds W.N. (1973) CF Structure and Physical Properties, in: Chemistry and Physics of Carbon, vol.2, Midenhead, Berkshire, pp.2-68.

Schnabel, W., et al. (1984) LET in Radiolisis of Polymers Macromolecules, 17, 2108-2111.

Schön,J. et al.(2000) DCB Delamination Behavior…, Composite Science and Technology 60 (2) 173-184

Sekulic, D.R. et al. (2009, Effects of Gamma Irradiation and Annealing…, 383 (3) 209-214.

Sekulic, D.R. & Stevanovic, M.M. (2011) Effects of gamma irradiation and annealing…, Journal of Nuclear Materials,

412 (1) 190-194.

Tidestrom, S.H. (1959) Manuel de base de l'ingenieur, Tome I, Dunod, Paris, pp.136-151.

Yates, B.W. & Shinozaki, D.M. (1993) PMC Radiation degradation, Journal of Polymer Science 31, 1779 – 1784.

**MOMCILO STEVANOVIĆ,** full member of Accademy of Engineering Science of Serbia**,** retired scientific counselor and full professor. He was born in 1935, and done Ph.D. thesis in 1965, at Faculty of Chemical Engineering, Belgrade. He has done his post graduated studies performed in CEN Saclay (1962-1964), post doctoral studies in AB Atomenergi Studswik, Sweden (1966) and in CEN Saclay. Up to the end of 2005, he has worked in Materials Department (Institute of Nuclear Sciences Vinča), since 1967 as scientific associate, since 1977 as senior scientific associate and since 1986 as scientific counselor. Besides, he has engaged: a) as assistant professor (Faculty of Electronic Engineering, Nis) (1969-1973); b) as associate professor and full professor (Faculty of Chemical Engineering, Novi Sad, (1975-1982) and c) as full professor at Chemical Engineering Faculty in Belgrad (1996-2000).

Stevanovic has been leader of several research and development projects. He was head of Ceramic Section (1971-1973), head of Materials Department (1974-1975) and the Deputy of General Director in Vinca Institute (1986-1990) He was member of Vinca Institute Scientific Comity and vice president of Institute Director Comity (1994-1998). He has for a long time member of Serbian Chemical Society, chairman of Ceramic Commission of Yugoslav Chemical Societies Union in period 1974-1977. He is the member of Material Research Society, and as well he was member of International Societies for Composite Materials: International Community of Composite Materials-New Orleans (since 1994) and European Society for Composite Materials (since 1998) and American Nano Society (since 2012). In 2005 he was elected member of Scientific Society of Serbia, in 2007 corresponding and in 2009 full membre of Academy of Engineering Sciences of Serbia.

In the first half of his working period, he has engaged in research related to ceramic oxide materials: (radiation damage; high temperature processes of mass transport, non stoishiometry of uranium dioxide; thermodynamics of vapor-liquid and vapor-solid equilibrium). In the second half of his working period, he has been dedicated to the study of mechanics of composite materials. (non linear elasticity of carbon fibers; edge and size effects; effects of irradiation,; delamination strain energy release rate and nanoidentation properties; strength analysis, micro-fractographic analysis).

Stevanovic has publisahed more than 200 publications, including 2 scentific monographs, 4 university text books, 47 papers in international journals (14 in leading international ones). Hi has been honored by medallion awarded to 25 most eminent Vinca Institute associates on the occasion of fiftieth anniversary of Institute foundation.